

7.3. Electrons in Solids

7.3.1. Free electrons in three-dimensions

Consider free electrons confined to a volume $V = L_1 L_2 L_3$.
 The wavefunction of the electron is a solution of Schrödinger equation:

$$\boxed{-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) = E \psi(\vec{r})}$$

$$\nabla^2 \psi + \left(\frac{2mE}{\hbar^2}\right) \psi = 0.$$

General solution: $\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}}$ $(k^2 = \frac{2mE}{\hbar^2})$

Periodic Boundary Condition: $\psi(\vec{r} + \vec{L}) = \psi(\vec{r})$ $(\vec{L} = L_1 \hat{i} + L_2 \hat{j} + L_3 \hat{k})$

therefore: $e^{i\vec{k} \cdot (\vec{r} + \vec{L})} = e^{i\vec{k} \cdot \vec{r}}$
 i.e.: $e^{i\vec{k} \cdot \vec{L}} = 1$

or: allowed wavevector:
$$\begin{cases} k_x = 0, \pm \frac{2\pi}{L_1}, \pm \frac{4\pi}{L_1}, \dots & \left(\pm \frac{2n\pi}{L_1}\right) \\ k_y = 0, \pm \frac{2\pi}{L_2}, \pm \frac{4\pi}{L_2}, \dots & \left(\pm \frac{2n\pi}{L_2}\right) \\ k_z = 0, \pm \frac{2\pi}{L_3}, \pm \frac{4\pi}{L_3}, \dots & \left(\pm \frac{2n\pi}{L_3}\right) \end{cases}$$

(quantum number)

and: $E_k = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$

Energy
 (allowed energy states/levels)

* Properties of Free electrons in solids

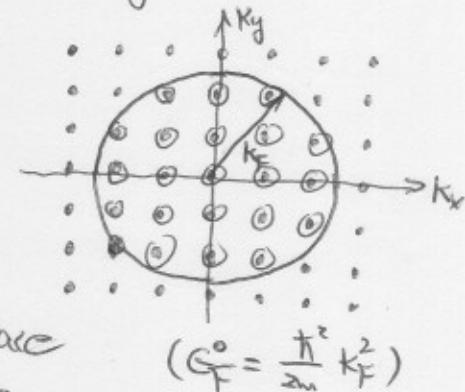
① Fermi energy E_F^o (at ground state)

E_F^o is defined as the energy of the top-most filled energy level in the ground state of N -electron system.

In \vec{k} -space:

- there is one allowed wavevector \vec{k} per \vec{k} -space volume $\frac{8\pi^3}{L_1 L_2 L_3} = \frac{8\pi^3}{V}$
- each \vec{k} takes \vec{k} -space volume $\frac{8\pi^3}{V}$
- there are $\frac{V}{8\pi^3}$ allowed wavevectors per unit \vec{k} -space
- total number of wavevectors with $k < k_F$ is:

$$\underbrace{\frac{4}{3}\pi k_F^3 \cdot \left(\frac{V}{8\pi^3}\right)}_{\vec{k}\text{-space volume}}$$



In the ground state, N electrons will occupy the energy levels as:

$$N = 2 \cdot \left(\frac{4}{3}\pi k_F^3 \right) \cdot \left(\frac{V}{8\pi^3} \right)$$

due to spin

(each allowed \vec{k} state can have $2 e^-$)

Therefore:

$$k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3}$$

And:

$$E_F^o = \frac{\pi^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

② Equilibrium distribution of electrons:

$$f_{FD}(\epsilon) = \frac{1}{e^{\frac{\epsilon - E_F}{k_B T}} + 1}$$

Fermi - Dirac distribution.

③ Density of electron states $D(\epsilon)$

$D(\epsilon)$: The number of electron orbitals (energy states/levels) per unit energy range.

- The number of orbitals with wavevector smaller than k is:

$$N_{(<k)} = 2 \cdot \left(\frac{4}{3} \pi k^3 \right) \cdot \left(\frac{V}{8\pi^3} \right)$$

- The number of orbitals with energy smaller than ϵ is:

$$N_{(<\epsilon)} = 2 \cdot \left(\frac{4}{3} \pi \underbrace{\left(\frac{2m\epsilon}{\hbar^2} \right)^{3/2}}_{\approx k} \right) \cdot \left(\frac{V}{8\pi^3} \right) = \frac{V}{3\pi^2} \left(\frac{2m\epsilon}{\hbar^2} \right)^{3/2}$$

- the density of states:

$$D(\epsilon) = \frac{dN_{(<\epsilon)}}{d\epsilon} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \cdot \epsilon^{1/2}$$

i.e., $D(\epsilon) = C \epsilon^{1/2}$

7.3.2. Electron heat capacity of solids.

* The total number of electrons: ($T > 0K$)

$$\underbrace{N = \int_0^{\infty} D(\epsilon) f(\epsilon) d\epsilon}$$

considering: $D(\epsilon) = C e^{-\frac{\epsilon}{kT}}$

$$\begin{aligned} \text{so: } N &= \int_0^{\infty} C f(\epsilon) e^{-\frac{\epsilon}{kT}} d\epsilon \\ &= \cancel{\frac{2}{3} C f(0) \epsilon^{\frac{3}{2}} \Big|_0^{\infty}} - \frac{2}{3} C \int_0^{\infty} \epsilon^{\frac{3}{2}} \frac{\partial f}{\partial \epsilon} d\epsilon \\ &= -\frac{2}{3} C \int_0^{\infty} \epsilon^{\frac{3}{2}} \frac{\partial f}{\partial \epsilon} d\epsilon \end{aligned}$$

$\frac{\partial f}{\partial \epsilon}$ can be expanded (Taylor series) about ϵ_F

The result:

$$\overline{N} \approx \frac{2}{3} C \epsilon_F^{\frac{3}{2}} \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\epsilon_F} \right)^2 \right]$$

$$\text{and: } \epsilon_F = \epsilon_F^0 \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\epsilon_F^0} \right)^2 \right]$$

* The total energy of electrons:

$$\overline{U} = \int_0^{\infty} \epsilon D(\epsilon) f(\epsilon) d\epsilon$$

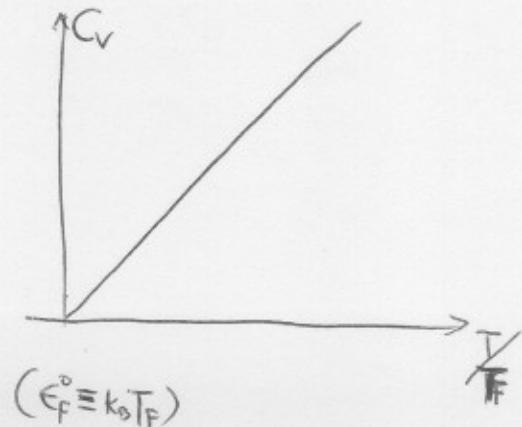
The result:

$$\overline{U} \approx \frac{3}{5} N \epsilon_F^0 \left[1 + \frac{5}{12} \pi^2 \left(\frac{k_B T}{\epsilon_F^0} \right)^2 \right]$$

* The electron heat capacity:

$$\overline{C_V} = \left(\frac{\partial \overline{U}}{\partial T} \right)_V \approx \frac{\pi^2}{2} N k_B \frac{k_B T}{\epsilon_F^0}$$

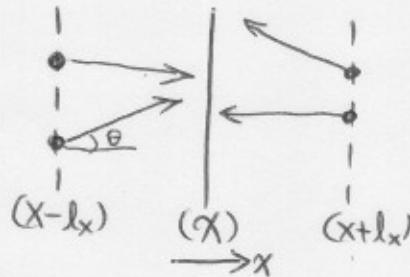
(For $k_B T \ll \epsilon_F^0$)



7.4. Thermal Conductivity.

- * Scattering of microscopic energy carriers (e.g. phonons and electrons) gives rise to resistance to energy transport.
(If there were no collision/scattering, the heat flux would not depend on the temperature gradient.)
- * Mean free path l : the average distance an energy carrier can travel before collision with other carriers (particles).
- * Derivation of κ (thermal conductivity).

Consider a plane at x , across which microscopic particles travel from either side. Consider two additional planes at $x \pm l_x$, here l_x is the x -component of the mean free path.



Assuming the particles have a mean velocity v , the net flux of energy across plane x in x -direction is:

$$\dot{Q}_x = \frac{1}{2} u(x-l_x) \cdot v_x - \frac{1}{2} u(x+l_x) \cdot v_x$$

$\left\{ \begin{array}{l} v_x \text{ is the } x\text{-component of } v \\ u(x \pm l_x) \text{ is the energy carried by particles at plane } x \end{array} \right.$

$\left\{ \begin{array}{l} v_x = v \cos \theta \\ l_x = l \cos \theta \end{array} \right.$

Using Taylor expansion, we have:

$$\dot{Q}_x = -v_x l_x \frac{du}{dx} = -(cos^2 \theta) v l \frac{du}{dx}$$

$$\left\{ \begin{array}{l} v_x = v \cos \theta \\ l_x = l \cos \theta \end{array} \right.$$

Averaging over $\theta: 0 \rightarrow \frac{\pi}{2}$, we have,

$$\tilde{q}_x = -\frac{1}{3}cvl \frac{du}{dx}$$

Assuming internal energy u is only a function of T ,

so: $\tilde{q}_x = -\frac{1}{3}cvl \frac{dT}{dx}$ $(du = cdt)$
 heat capacity.

i.e.:
$$K = \frac{1}{3}cvl$$
 | thermal conductivity.

Considering the contribution from phonons and electrons:

$$K = \frac{1}{3} [(cvl)_{ph} + (cvl)_{el}]$$

↑
phonon
contribution ↑
electron
contribution.

and:

$$\tilde{q}_x = -K \frac{dT}{dx}$$

Fourier Law.